Molecular Dynamics for Elastic and Plastic Deformation of a Single-Walled Carbon Nanotube Under Nanoindentation *

FANG Te-Hua(方得华)[1]**, JIAN Sheng-Rui(简胜瑞)[2], CHUU Der-San(褚德三)[2]

[1]*Department of Mechanical Engineering, Southern Taiwan University of Technology, Tainan 710*
[2]*Institute and Department of Electrophysics, National Chiao Tung University, Hsinchu 300*

Mechanical characteristics of a suspended $(10, 10)$ single-walled carbon nanotube (SWCNT) during atomic force microscopy (AFM) nanoindentation are investigated at different temperatures by molecular dynamics simulations. The results indicate that the Young modulus of the $(10, 10)$ SWCNT under temperatures of 300–600 K is 1.2–1.3 TPa. As the temperature increases, the Young modulus of the SWCNT increases, but the axial strain of the SWCNT decreases. The strain-induced spontaneous formation of the Stone–Wales defects and the rippled behaviour under inhomogeneous stress are studied. The rippled behaviour of the SWCNT is enhanced with the increasing axial strain. The adhesive phenomenon between the probe and the nanotube and the elastic recovery of the nanotube during the retraction are also investigated.

PACS: 61. 46. +w, 62. 20. −x, 81. 07. De

Since the discovery of single-walled carbon nanotubes (SWCNTs) in 1993,[1] their remarkable electrical properties have made them ideal for applications in the fabrication of nanoelectronics devices.[2] SWCNTs exhibit interesting characteristics such as high-strength, high Young's modulus of 1 TPa and the ability to sustain large strain for potential applications in nanotechnology.[3,4] Recently, Walters *et al.*[5] have measured the elastic strain and elastic moduli of SWCNT ropes using an atomic force microscopy (AFM) probe. Minot *et al.*[6] found that the mechanical and electrical properties of nanotubes could be affected by contact deformation with an AFM probe. To address deeply the characteristics, molecular dynamics (MD) has been employed to analyse the complex nanomechanisms.[7,8] We present MD studies of the temperature influence on nanomechanical behaviour during the indentation and retraction between an AFM probe and a suspended $(10, 10)$ SWCNT.

MD simulation with the Tersoff potential[9] is adopted to study the bending behaviour of a suspended $(10, 10)$ SWCNT and solve Hamilton's equations of motion with Gear's fifth predictor-corrector method[10] with a time step of 1 fs. A pyramid Si(100) probe and a $(10, 10)$ SWCNT with a diameter of 1.4 nm contain 214 and 1600 atoms, respectively. The MD model is illustrated in Fig. 1. The atoms in the two ends of the carbon nanotube are fixed in space. The indentation and the retraction are performed at a loading rate of 50 m/s under temperatures of 300–600 K. The velocity of the atoms at a constant temperature is satisfied with Maxwell's velocity distribution and the NVT model[10] is used to control the number of atoms N, volume V and temperature T.

The characteristic of force F_z of the bent nanotube versus displacement d at various temperatures is depicted in Fig. 2. At the initial case, $d = 0$, the probe approaches the nanotube and the attractive force between the probe and the tube occurs. This adhesion has been observed and discussed in previous experimental study.[6] The nonlinear behaviour in the force curves is evidence of the nanotube inelastic response. The points of P, A_3, Q and R display the cleavage behaviour of the nanotube and represent the relationships between the strength of the nanotube and the temperatures. It is observed that the vibration of the SWCNT is in the axial direction. The vibration frequency for a $(10, 10)$ SWCNT is in agreement with the previous experimental values of 4.9×10^3 GHz.[11] The temperature manifests no
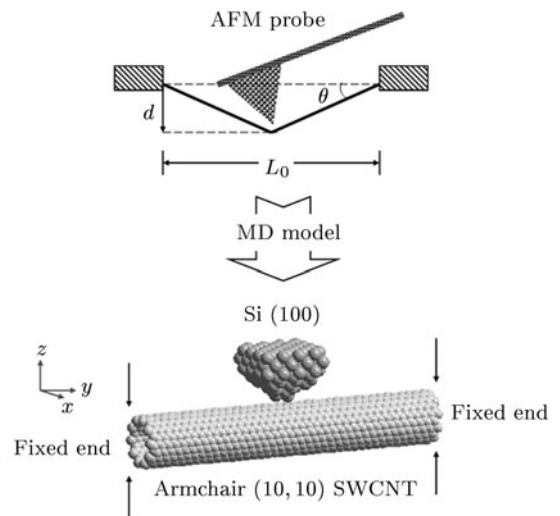
Fig. 1. Schematic of the MD simulation model for a Si(100) AFM probe and an armchair $(10, 10)$ SWCNT. L_0 is the distance between the two terminals; d is the downward displacement from the centre of the SWCNT.

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change of the vibration frequency in the nanotube. The deformation corresponding to the nanotube bending at a temperature of 400 K is shown in the inset of Fig. 2 and the abraded probe can be observed. As the probe approaches the graphite layer of the nanotube, the corrugate phenomenon develops in the lateral direction on the nanotube and causes irreversible deformation. The bond-breaking occurs at both the ends of the nanotube symmetrically at higher axial strain as shown in Fig. 2 (A_3). This is because the AFM probe indented the neck of nanotube and subsequently shear force was caused at the end of the nanotube. The abraded probe atoms have a crystalline order different from that of the original silicon pyramidal probe structure. This phenomenon was also found in AFM experiments.[12] To measure the Young modulus of a 'single' $(10, 10)$ SWCNT, the Minot method[6] is adopted. Young's modulus under temperatures of 300–600 K is about 1.2–1.3 TPa. The results are in agreement with the previous studies which pointed out that Young's modulus could be affected by several factors such as the chosen potential[13] and the procedures used to apply the strain.[14]
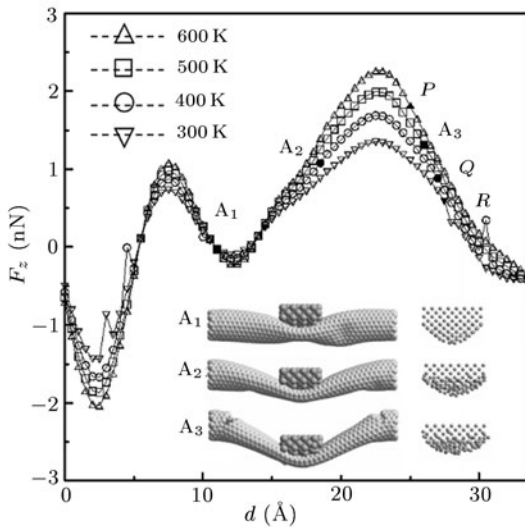

Fig. 2. Force F_z from the carbon nanotube induced by AFM nanoindentation at various temperatures.

The structural changes of a $(10, 10)$ SWCNT during nanoindentation under various temperatures are further illustrated using radial distribution function (RDF) analysis[10] and are shown in Fig. 3. With an increase of specific positions r, the RDF peaks reduce in magnitude and slightly shift to a smaller value of r due to the compressed C–C bonds parallel to the nanotube axis. At a higher temperature state or higher axial strain, there manifests a change in the structure of the nanotube. The bond-breaking extends around the circumference and implies that the long-range order of the C–C bond is broken, leading to form the cleavage events at the ends of the nanotube. The fracture strain ε_f of the $(10, 10)$ SWCNT for the temper-

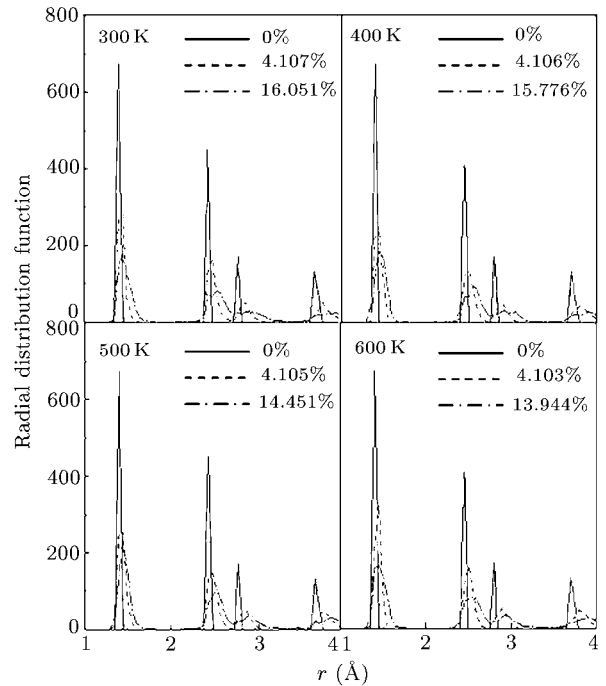atures of 300, 400, 500 and 600 K is 16.1%, 15.8%, 14.5% and 13.9%, respectively.

Fig. 3. Radial distribution function (RDF) of SWCNT at various temperatures during nanoindentation.

Figure 4 shows the strain energy of a $(10, 10)$ SWCNT as a function of the axial strain at temperatures of 300–600 K. The critical axial strain for 300, 400, 500 and 600 K is 15.5% (up-down triangles), 15.1% (circles), 14.1% (squares) and 13.8% (triangles), respectively. It can be seen that Hooke's law holds for a SWCNT (initially responds quasi-elastically) until the tube reaches a critical axial strain. By increasing the temperature of the system, a strong anisotropy of the thermal expansion properties in the axial and radial directions results in the change of the critical point. The maximum bending strength of a $(10, 10)$ SWCNT is 1.5–1.8 TPa under temperatures of 300–600 K and decreases with increase of temperature. The higher the temperature, the easier it was to break the ends of the nanotube. During the indentation process, the Stone–Wales defect[15] occurs, resulting in the double pentagon-heptagon pair defect at an axial strain of 0.7%. The inset of Fig. 4 shows the various stages of the topological defect formation, which takes about 19.1 ps under a temperature of 300 K. The slight plastic flow behaviour appears at 50.0 ps and at an axial strain of 10.2%. It is evident that the indentation-induced inhomogeneous stress causes the corrugated phenomenon laterally surrounding the nanotube and causes the formation of the topological defect at the ends of the nanotube. The topological defect leads to the nanotube displaying flexibility, and the cleavage behaviour easily occurs at higher temperature.
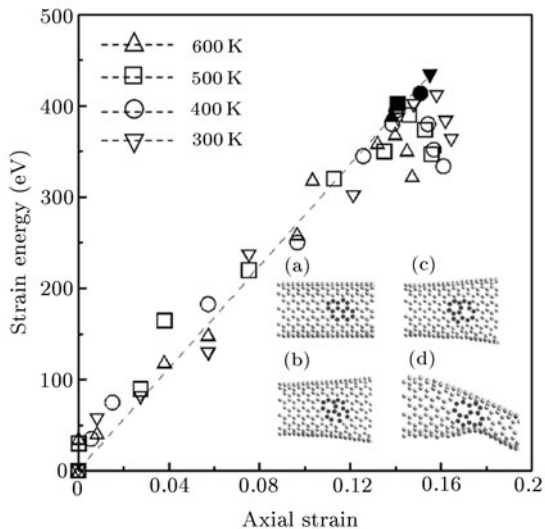
Fig. 4. The strain energy versus the axial strain at various temperatures.
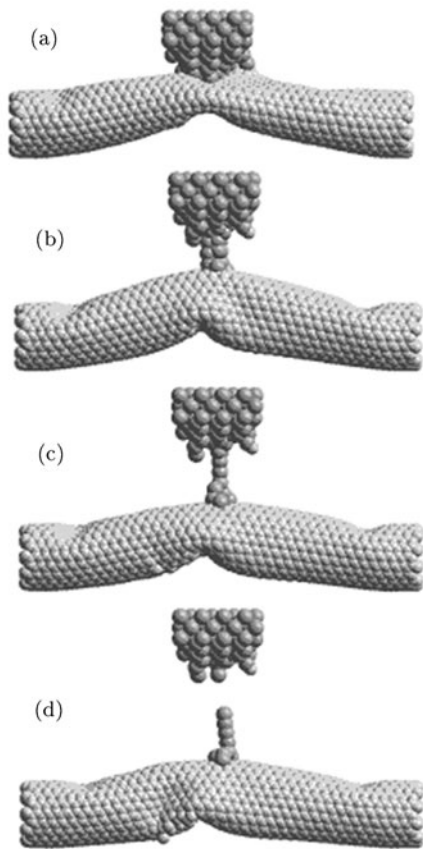

Fig. 5. Atomic configurations corresponding to the withdrawal stages of SWCNT at 400 K: (a) 54 ps, (b) 79 ps, (c) 82 ps, and (d) 100 ps.

Figure 5 shows the atomic configurations during the retraction process at a temperature of 400 K. The adhesion between the probe and the nanotube and the nanotube's elastic recovery are observed. The corrugated phenomenon can also occur during the retraction of the probe. Once the elastic force of the nanotube overcomes the probe/nanotube adhesion force, the Si–C chain will be broken, resulting in leaving some of the probe atoms on the nanotube surface. This behaviour is similar to that of the previous studies.[16] Upon retraction of the AFM probe, the formation of the connective neck elongates appreciably [Figs. 5(b)–5(c)] and eventually ruptures [Fig. 5(d)]. The Si–C chain is more observed at higher temperature, the nanotube/probe adhesion force increases with the increasing temperature and the adhesion is strong enough to induce the bending behaviour and the elongation of the nanotube surface at the point of indentation/retraction.

In summary, we have investigated the mechanical characterizations of a suspended (10, 10) SWCNT during the indentation and retraction process. The results indicate that Young's modulus of the (10, 10) SWCNT increases from 1.2 to 1.3 TPa with the increasing temperature. The maximum bending strength and the critical axial strain are evaluated to be 1.5–1.8 TPa and 13.8–15.5%, respectively. The spontaneous formation of Stone–Wales defects has been observed in the strained nanotube. Upon retraction of the AFM probe, the local deformed region of the nanotube would experience an incomplete elastic recovery, signifying that the plastic nature of rearrangement is accompanied by the corrugated behaviour surrounding the nanotube.

References

[1] Iijima S and Ichihashi T 1993 *Nature* **363** 603
[2] Duan X F, Huang Y, Cui Y, Wang J F and Lieber C M 2001 *Nature* **409** 66
[3] Yu M F, Files B S, Arepalli S and Ruoff R S 2000 *Phys. Rev. Lett.* **84** 5552
[4] Ozaki T, Iwasa Y and Mitani T 2000 *Phys. Rev. Lett.* **84** 1712
[5] Walters D A, Ericson L M, Casavant M J, Liu J, Colbert D T, Smith K A and Smalley R E 1999 *Appl. Phys. Lett.* **74** 3803
[6] Minot E D, Yaish Y, Sazonova V, Park J Y, Brink M and McEuen P L 2003 *Phys. Rev. Lett.* **90** 156401
[7] Fang T H, Jian S R and Chuu D S 2002 *Jpn. J. Appl. Phys.* **41** L1328
[8] Fang T H, Weng C I and Chang J G 2002 *Surf. Sci.* **501** 138
[9] Tersoff J 1988 *Phys. Rev. Lett.* **61** 2879
Tersoff J 1989 *Phys. Rev.* B **39** 5566
[10] Haile J M 1992 *Molecular Dynamics Simulation: Elementary Method* (New York: Wiley)
[11] Rao A M, Richter E, Bandow S, Chase B, Eklund P C, Williams K A, Fang S, Subbaswamy K R, Menon M, Thess A, Smalley R E, Dresselhaus G and Dresselhaus M S 1997 *Science* **275** 187
[12] Bhushan B and Koinkar V N 1994 *J. Appl. Phys.* **75** 5741
[13] Zhou G, Duan W and Gu B 2001 *Chem. Phys. Lett.* **333** 344
[14] Xia Y, Zhao M, Ma Y, Ying M, Liu X and Nei L 2002 *Phys. Rev. Lett.* **65** 155415
[15] Yakobson B I 1998 *Appl. Phys. Lett.* **72** 918
[16] Young C W, Smith W and Kendall K 2003 *Nanotechnol.* **14** 829